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Study of possibility of cerium reduction from slags of CaO-SiO_2-Ce_2O_3– 15%Al_2O_3– 8%MgO system

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Abstract. By means of theoretical and experimental studies it is shown that it is possible to reduction cerium from the slags of the CaO–SiO_2–Ce_2O_3 system containing 15%Al_2O_3 and 8 % MgO, by aluminum dissolved in metal, at temperatures of 1550 and 1650°C. The results of mathematical modeling are presented graphically as 'composition – equilibrium content of cerium in metal' diagrams. It is found that depending on temperature of metal, basicity of slag and the content of cerium oxide, from 0.055 to 16 ppm cerium passes into metal containing 0.06 % of carbon, 0.25 % of silicon and 0.055 % of aluminium. Positive influence of the temperature factor, basicity of slags and the content of cerium oxide in a studied range of chemical composition on process of cerium reduction is explained from the perspective of phase structure of formed slags and thermodynamics of reactions of cerium reduction. The possibility of reduction of cerium from slags of CaO–SiO_2–Ce_2O_3 system, containing 15 % Al_2O_3 and 8 % MgO, has been experimentally confirmed. It has been shown that at basicity of 5 and 4 % of Ce_2O_3 in slag up to 16 ppm cerium passes into metal during 10 minutes exposure.

1. Introduction

Due to the increase in construction of long gas main pipelines in Russia the research and development of composition of high-strength pipe steels and innovative technological solutions for their production are becoming more and more important for the domestic metallurgy. The promising way of solving the problem is steel microalloying with boron [1–6]. Microalloying of low-carbon boron steel is used to increase the set of mechanical, technological and operational properties while maintaining economically alloyed chemical composition. However, the conditions under which pipelines are laid and operated are characterized, as a rule, by cold climate and high seismic activity, therefore along with high strength the pipe steels have high requirements to impact toughness at low temperatures and deformation ability. However, the ductility of low-carbon steels is related to the impact toughness, the increase in which is accompanied by a decrease in both relative elongation and contraction. One of the directions for solving the problem of maintaining of high strength and providing plasticity of low-carbon steel is organization of the process of modification of metal with rare-earth metals (REM). Positive influence of REM on ductility, impact toughness and resistance to cyclic cracking of pipe steel has been repeatedly confirmed by studies [7–11].

It is known that ferroalloys are used to modify steel with REM. It leads to an increase in the cost of steel. One of the directions of the problem solving can be REM reduction from oxide systems. It is known that introduction of Ce_2O_3 into the refining slag reduces the activity of harmful Al_2O_3 inclusions in the metal, melting temperature and slag viscosity, as well as increases the desulfurization degree [12–18]. In addition, the possibility of reduction of cerium from the slags of the studied oxide system and its dissolution in steel in an amount up to 4ppm is noted, thus providing the effect of steel modification. The microstructure of the molten metal is better refined and consists of ferrite and a small amount of perlite [13–16].

Theoretical and experimental studies of the possibility of cerium reduction by aluminium dissolved in metal from the slags of the $CaO–SiO_2–Ce_2O_3–15\%Al_2O_3–8\%MgO$ system at temperatures of 1550 and 1650 °C are presented.

2. Materials and methods

The thermodynamic modeling of cerium reduction from slags of the $CaO–SiO_2–Ce_2O_3$ system containing 15% Al_2O_3 and 8% MgO, by aluminum dissolved in metal at temperatures of 1550 and 1650°C was performed using HSC 8.03 Chemistry (Outokumpu) software package based on Gibbs energy minimization and variational principles of thermodynamics using simplex planning grid method [19–22]. The principle of the method of simplex planning grids is to build a planning matrix, where the basicity of slag and Ce_2O_3 content in slag are changed (Table 1) with the following construction, on the basis of thermodynamic calculations, of mathematical model describing dependence of equilibrium Ce_2O_3 content in metal on slag composition, presented as diagrams 'the chemical composition of slags of the $CaO–SiO_2–Ce_2O_3$ system containing 15% Al_2O_3 and 8% MgO–equilibrium content of cerium in metal' at temperatures of 1550°C and 1650°C (Figures 1 and 2). In diagrams blue lines indicate isolines of equilibrium content of cerium. Thin black lines indicate the basicity of slag (B=CaO/SiO_2), the figures indicate their values.

Table 1. Slag composition and the results of thermodynamic modeling of the equilibrium cerium content in metal.

№	Slag index	Slag composition, mas. %					[Ce], ppm		B=CaO/SiO_2
		CaO	SiO_2	Ce_2O_3	Al_2O_3	MgO	1550ºC	1650ºC	
1	Y_1	50.7	25.3	1	15	8	0.055	0.085	2
2	Y_2	63.3	12.7	1	15	8	1.89	2.68	5
3	Y_3	58.3	11.7	7	15	8	11.7	16.1	5
4	Y_4	46.7	23.3	7	15	8	0.42	0.64	2
5	Y_{13}	59.1	16.9	1	15	8	0.72	1.03	3.5
6	Y_{132}	56	16	5	15	8	3.47	4.94	3.5
7	Y_{22}	60	12	5	15	8	8.77	12.2	5
8	Y_{12}	54.9	21.1	1	15	8	0.23	0.34	2.6
9	Y_{121}	53.2	20.8	3	15	8	0.65	0.95	2.6
10	Y_{21}	61.6	12.4	3	15	8	5.43	7.61	5
11	Y_{131}	57.5	16.5	3	15	8	2.09	3.00	3.5
12	Y_{41}	48	24	5	15	8	0.29	0.44	2
13	Y_{31}	54.5	15.5	7	15	8	4.85	6.87	3.5
14	Y_{42}	49.4	24.6	3	15	8	0.17	0.26	2
15	Y_{32}	50.5	19.5	7	15	8	1.62	2.36	2.6
16	Y_{122}	51.9	20.1	5	15	8	1.13	1.66	2.6

Experimental studies on reduction of cerium from slag were carried out on the high-temperature unit, made on the basis of the Tamman resistance furnace. Slag from the $58\%CaO–12\%SiO_2–4\%Ce_2O_3–15\%Al_2O_3–8\%MgO$ system was used as an experimental slag. Steel containing 0.06 % carbon, 0.25% silicon and 0.05% aluminum was used as metal. A 90 g sample of metal and 9 g slag (10 % of the metal weight) was loaded into a corundum crucible and installed in a furnace, heated and melted. The molten metal and slag were heated up to 1650°C and kept in the crucible for 10 min. Four parallel experiments were carried out with metal hot soak under the slag of the abovementioned composition in the crucible for 10 min.

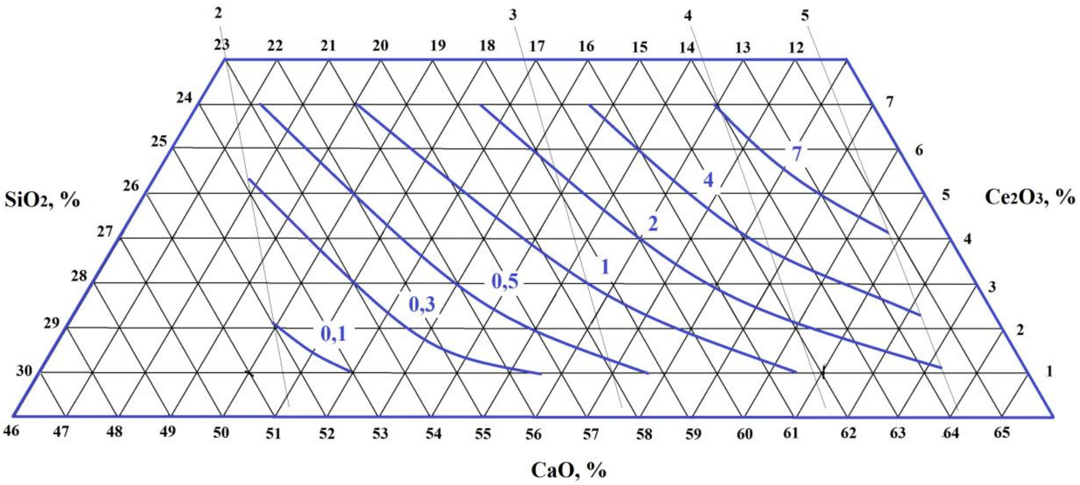

Figure 1. Diagram of the equilibrium content of cerium in metal hot-soaked under the slag of the CaO–SiO_2–Ce_2O_3 system containing 15% Al_2O_3 and 8% MgO at the temperature of 1550°C.

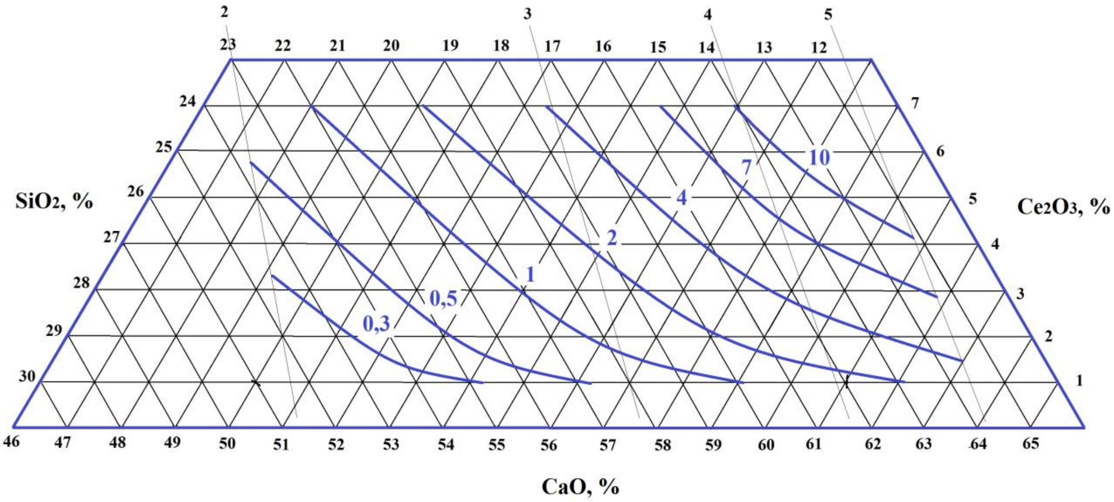

Figure 2. Diagram of the equilibrium content of cerium in metal hot-soaked under the slag of the CaO–SiO_2–Ce_2O_3 system containing 15% Al_2O_3 and 8% MgO at the temperature of 1650°C.

Results and discussion

Depending on temperature of metal, basicity of slag and the content of cerium oxide at the expense of the chemical reactions presented in Table 2, from 0.055 to 16 ppm cerium passes into metal. Thus hot soak of the metal containing 0.06 % C, 0.25 % Si and 0.055 % Al, under slag basicity of 2.0, containing 1.0 % cerium oxide, up to 0.055 ppm cerium passes into metal at temperature of 1550 °C. Increase of temperature of system to 1650°C is accompanied by insignificant increase in cerium concentration reaching no more than 0.085 ppm. At increase to 7.0 % of cerium oxide concentration in slag with basicity of 2.0 more essential increase of the content of cerium in metal is observed, reaching in a range of temperatures 1550–1650°C 0.4–0.6 ppm, accordingly.

The growth of basicity of slag favourably affects development of process of reduction of cerium. The increase in basicity of slag from 2 to 5 leads to the increase of the equilibrium content of cerium in the metal from 0.1 to 7 ppm at a temperature of 1550°C (Figure 1). Thus, with temperature increase to 1650°C the equilibrium content of cerium in metal increases and changes in a considered range of basicity of slag on the average from 0.3 up to 10 ppm (Figure 2).

Table 2. Gibbs energy change for chemical reactions of cerium reduction.

№	Chemical reactions	Δ*G*, kJ/mol	
		1550°C	1650°C
1	$2Ce_2O_3 + 6Al = CeAlO_3 + 2CeAl_2$	–173	–164
2	$CeAlO_3 + 2Al + 3CaO = Ca3Al2O6 + 2CeAl_2$	–83	–84
3	$CeAl_2 + 1.5SiO_2 = Al_2O_3 + Ce + 1.5Si$	–93	–91
4	$3CeO_2 + 4Al + 6CaO = 3Ce + 2Ca_3Al_2O_6$	–226	–233

According to the data given in the Table 2 aluminum dissolved in metal interacts with cerium oxides Ce_2O_3, CeO_2 and cerium aluminate $CeAl_2O_3$ by reactions 1, 2 and 4 with the formation of cerium aluminide $CeAl_2$, tri-calcium aluminate and metallic cerium. Cerium aluminide $CeAl_2$ interacting with silicon oxide SiO_2 by the reaction 3 provides the formation of aluminum oxide Al_2O_3 in the slag, cerium and silicon in the metal. However low concentrations of free cerium oxides Ce_2O_3, CeO_2, which do not exceed 0.009 and 0.005%, and free calcium oxide CaO, which do not exceed 2.5 %, in slags formed in the region of reduced to 2.0 basicity and containing no more than 1.0% of cerium oxide, do not provide proper development of the reactions given in Table 2 and, as a consequence, do not provide high concentrations of cerium in metal as well (Table 1). Observed insignificant increase in concentration of cerium in metal with increase in temperature of metal and concentration of free cerium oxides Ce_2O_3, CeO_2, reaching 0.05 and 0.007 %, apparently is caused by development of reactions 2 and 4. Increase in basicity of formed slags to 5.0 is accompanied by increase in concentration of free calcium oxide CaO to 24 % and, as consequence, increase in equilibrium concentration of cerium in metal (Table 1) at the expense of development of reactions 2 and 4.

Hot soak of metal containing 0.06% carbon, 0.25% silicon and 0.05% aluminum under slag containing 58% CaO, 12% SiO_2, 15% Al_2O_3, 8% MgO and 4% Ce_2O_3 is accompanied by reduction of cerium, the concentration of which after 10 minutes of hot soak approaches 16 ppm cerium. At the same time, experimental data practically confirm the results of thermodynamic modeling.

3. Conclusions

It is found that from 0.055 to 16 ppm cerium content passes in the steel, containing 0.06% carbon, 0.25 % silicon and 0.05% aluminum, depending on the metal temperature, basicity of slag and cerium oxide. Thermodynamic modeling together with the method of simplex planning grids allowed to obtain new data on the equilibrium content of cerium in a metal containing 0.06% C, 0.25% Si, 0.05 % Al, hot soaked under the slag of the $CaO–SiO_2–Ce_2O_3–15\%Al_2O_3–8\%MgO$ system in a wide range of chemical compositions at temperatures of 1550°C and 1650°C. The results of thermodynamic modeling have been experimentally confirmed.

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